

BEHAVIOUR OF GASES

INTRODUCTION :

Gaseous state is that state of matter where repulsive forces are dominating than attractive forces. For study of gases we require gas parameters like p, v, n and temperature. Gases having no interaction between gas molecules are known as ideal gases. They follow kinetic gas assumptions, kinetic gas equation, gas laws and ideal gas equation but certain gases which do not follow above conditions are known as real gases.

(A) SOME IMPORTANT DEFINITIONS :

(a) Diffusion :

- The tendency of inter mixing of non-reacting gases spontaneously without external pressure.

or

- The property of the spontaneous flow of gaseous molecules from high concentration to low concentration without external pressure.

In diffusion, $P_{\text{ext}} = \text{constant}$.

(b) Effusion :

- The property of the flow of gaseous molecules from high concentration to low concentration from a **pin hole** with external pressure.

or

- It is diffusion through **pin hole** which arises due to pressure difference.

In effusion, $P_{\text{ext}} = \text{variable}$

(c) Rate of diffusion (r) :

At constant temperature and pressure, the distance travelled by diffused gas or volume of diffused gas or moles of diffused gas per unit time is called as rate of diffusion.

$$r = \frac{d_{\text{diffused gas}}}{t_{\text{(taken)}}} = \frac{V_{\text{diffused gas}}}{t_{\text{(taken)}}} = \frac{n_{\text{diffused gas}}}{t_{\text{(taken)}}}$$

Graham's law of diffusion (Applicable for non-reacting gases) :

- At constant temperature and pressure, the rate of diffusion is inversely proportional to the square root of the density.

$$r \propto \frac{1}{\sqrt{d}} \quad (\text{at constant T and P})$$

$$r \propto \frac{1}{\sqrt{VD}}$$

$$r \propto \frac{1}{\sqrt{M_w}}$$

$$\frac{r_1}{r_2} = \frac{v_1}{t_1} \times \frac{t_2}{v_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

- At constant temperature, rate of diffusion is proportional to $\frac{P}{\sqrt{d}}$.

$$\frac{r_1}{r_2} = \frac{v_1}{t_1} \times \frac{t_2}{v_2} = \frac{P_1}{P_2} \sqrt{\frac{d_2}{d_1}} = \frac{P_1}{P_2} \sqrt{\frac{M_2}{M_1}}$$



(B) REAL GASES : Those gases which do not follow ideal gas equation ($PV = nRT$) at all temperature and pressure.

• For real gases two assumptions of the kinetic theory do not hold good. These are

(i) There is no force of attraction between the molecules of a gas.

(ii) Volume of the molecules of a gas is negligibly small in comparison to the space occupied by the gas.

(a) REAL GAS EQUATION OR VAN DER WAAL GAS EQUATION

$$PV = nRT \quad \dots(1) \text{ ideal gas equation}$$

Two major corrections are required for real gases

(i) The intermolecular force of attraction between molecules is not negligible.

$$F_{\text{att}} \neq 0 \text{ so } P_{\text{act.}} = \left(P_{\text{real}} + \frac{n^2 a}{V^2} \right)$$

(ii) The volume of a molecule is not negligible in comparison of total volume of gas.

$$V_1 \neq 0 \text{ so } V_{\text{act}} = (V - nb)$$

$$b = \text{covolume} = \text{excluded volume} = 4 \times \frac{4\pi r^3}{3} \times N_A$$

From equation (i)

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

- a and b are van der Waal's gas constant which depends on nature of gas but do not depend on the temperature and pressure.

(A) van der Waal's gas constant (a) :

Where **a** is van der Waal gas constant which indicates the **inter molecular** forces of attraction.

$$\text{Pressure} = \frac{an^2}{V^2}$$

$$\text{unit of } a = \text{atm L}^2 \text{ mol}^{-2}$$

$$P_i = P_R + \frac{an^2}{V^2}$$

$$P_i > P_R$$

- $a \uparrow \Rightarrow F_{\text{att}} \uparrow \Rightarrow \text{liquefaction} \uparrow$.
- Order of a is 10^{-1} to $10^{-2} \text{ atm L}^2 \text{ mol}^{-2}$

(B) van der Waal gas constant (b)

It tells about molecular volume of gas molecules.

$$\text{Unit of } b = \text{L mol}^{-1}$$

b = incompressible volume

$$V_i > V_R$$

- If $b \uparrow \Rightarrow \text{effective size of molecule} \uparrow$
 $\Rightarrow \text{Incompressible volume} \uparrow$
 $\Rightarrow \text{compressible volume} \downarrow$
- Order of b is 10^{-2} to $10^{-4} \text{ L mol}^{-1}$



(b) DEVIATION OF REAL GASES FROM IDEAL GAS BEHAVIOUR :

"At very low pressure and high temperature real gases behave as ideal gas." Deviation of real gases from ideal gas behaviour is mathematically denoted by "Z" named as **compressibility factor**.

$$Z = \frac{V_{\text{real}}}{V_{\text{ideal}}} = \frac{V_{\text{obs}}}{nRT} = \frac{P(V_m)_{\text{obs}}}{RT}$$

Case I If $Z = 1$; ideal gas ; it signifies there is no interaction between gas molecules

$$\frac{P(V_m)_{\text{obs}}}{RT} = 1 \Rightarrow P(V_m)_{\text{obs}} = RT$$

Case II If $Z > 1$; positive deviation from ideal gas behaviour; signifies repulsive forces are greater than attractive forces so such gases can't be liquefied easily.

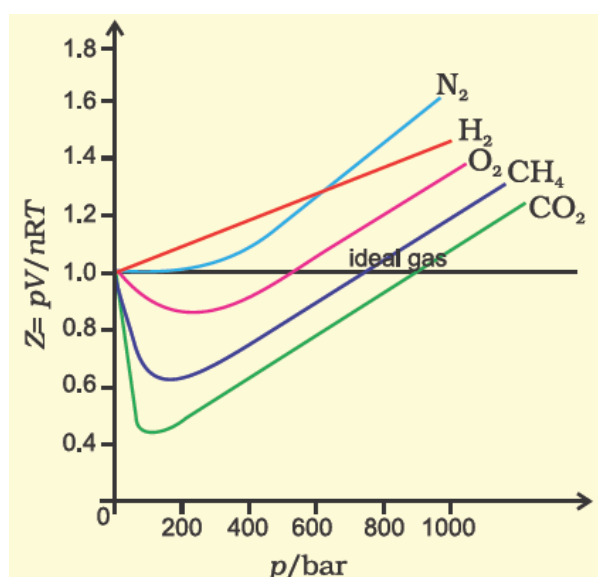
$$\frac{P(V_m)_{\text{obs}}}{RT} > 1 \Rightarrow P(V_m)_{\text{obs}} > RT$$

The gas shows the positive deviation generally at high pressure from ideal gas behaviour.

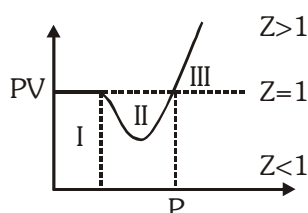
Case III If $Z < 1$; Negative deviation from ideal gases behaviour; it signifies attractive forces are higher than repulsive forces so gas can be liquefied easily.

$$\frac{P(V_m)_{\text{obs}}}{RT} < 1 \Rightarrow P(V_m)_{\text{obs}} < RT$$

The gas show the negative deviation generally at low pressure from ideal gas behaviour.



(c) Effect of pressure on van der Waal gas equation



Case I At very-very low pressure
(**Z = 1**)

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

$$PV = nRT$$

$$\frac{PV}{nRT} = 1$$

$$\boxed{Z = 1}$$

Case II At low pressure/moderate pressure
(**Z < 1**)

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

$$PV + \frac{n^2 a}{V} = nRT$$

$$\frac{PV}{nRT} + \frac{na}{VRT} = 1$$

$$\boxed{Z = 1 - \frac{na}{VRT}}$$

Case III At very high pressure
(**Z > 1**)

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

$$PV - nPb = nRT$$

$$\frac{PV}{nRT} + \frac{Pb}{RT} = 1$$

$$\boxed{Z = 1 + \frac{Pb}{RT}}$$

- At high temperature and low pressure, it acts as ideal gas equation.
- Critical temperature (T_c)** : The temperature below which gas can be liquefied by application of pressure

alone; is called critical temperature $\boxed{T_c = \frac{8a}{27bR}}$

- Critical pressure (P_c)** : The pressure required to liquefy a gas at critical temperature; is called critical pressure

$$\boxed{P_c = \frac{a}{27b^2}}$$



- Critical volume (VC) : Volume occupied by 1 mol gas at critical temperature & pressure; is called critical volume $V_c = 3b$.

- Van Der waal gas constants :

| Gas | a (atm L ² mol ⁻²) | b (L mol ⁻¹) |
|------------------|---|--------------------------|
| H ₂ | 0.244 | 0.0266 |
| N ₂ | 1.39 | 0.0391 |
| CH ₄ | 2.25 | 0.0428 |
| CO ₂ | 3.59 | 0.0427 |
| NH ₃ | 4.17 | 0.0371 |
| H ₂ O | 5.46 | 0.0305 |

- Higher value of "a" is more significant for liquefaction of a gas.
- **Boyle's Temperature (T_b)** : Temperature at which a real gas obeys ideal gas law over an appreciable range of pressure is called Boyle's temperature .

$$T_b = \frac{a}{bR}$$

Illustrations

Illustration 1 The rate of effusion of a gas is proportional to –

(1) $\frac{P}{\sqrt{d}}$ (2) $\frac{P}{d}$ (3) $\sqrt{\frac{P}{d}}$ (4) $\frac{\sqrt{P}}{d}$

Solution **Ans. (1)**

$$\text{Rate of effusion} \propto \frac{1}{\sqrt{d}} \propto P \therefore \text{Rate of effusion} \propto \frac{P}{\sqrt{d}}$$

Illustration 2 If 4g of oxygen diffuse through a very narrow hole, how much hydrogen would have diffused under identical conditions ?

(1) 16 g (2) 1 g (3) 1/4 g (4) 64 g

Solution **Ans. (2)**

$$\frac{r_{O_2}}{r_{H_2}} = \frac{V_{O_2}}{V_{H_2}} ; \frac{n_{O_2}}{n_{H_2}} = \sqrt{\frac{M_{wH_2}}{M_{wO_2}}} \Rightarrow \frac{4/32}{w/2} = \sqrt{\frac{2}{32}} \Rightarrow \frac{1}{4w} = \frac{1}{4} \Rightarrow w = 1$$

Illustration 3 van der Waal's equation of state is obeyed by real gases. For n moles of a real gas, the expression will be –

(1) $\left(\frac{P}{n} + \frac{na}{V^2}\right)\left(\frac{V}{n-b}\right) = RT$ (2) $\left(P + \frac{a}{V^2}\right)(V-b) = nRT$

(3) $\left(P + \frac{na}{V^2}\right)(nV-b) = nRT$ (4) $\left(P + \frac{n^2a}{V^2}\right)(V-nb) = nRT$

Solution **Ans. (4)**

$$\text{van der Waal's equation is } \left(P + \frac{an^2}{V^2}\right)(V-nb) = nRT$$



Illustration 4 van der Waal's constant 'a' and 'b' are related withrespectively –

- (1) Attractive force and bond energy of molecules
- (2) Volume and repulsive force of molecules
- (3) Shape and repulsive forces of molecules
- (4) Attractive force and volume of the molecules

Solution **Ans. (4)**

'a' is related to attractive forces and 'b' to the volume of the molecules.

BEGINNER'S BOX-1

1. The rate of diffusion of SO_2 and O_2 are in the ratio –
(1) $1 : \sqrt{2}$ (2) $1 : 32$ (3) $1 : 2$ (4) $1 : 4$
2. In the van der Waal's equation which will have highest value of 'a'.
(1) CH_4 (2) He (3) NH_3 (4) H_2
3. The unit of the van der Waal's constant 'a' is :
(1) $\text{atm L}^2 \text{ mol}^{-2}$ (2) $\text{atm L}^{-2} \text{ mol}^{-2}$ (3) atm L mol^{-1} (4) atm mol L^{-1}

ANSWER KEY

| BEGINNER'S BOX-1 | Que. | 1 | 2 | 3 | | | | | | | |
|------------------|------|---|---|---|--|--|--|--|--|--|--|
| | Ans. | 1 | 3 | 1 | | | | | | | |



EXERCISE-I (Conceptual Questions)**GRAHAM'S LAW OF DIFFUSION**

- Which pair of the gaseous species diffuse through a small jet with the same rate of diffusion at same P and T :
(1) NO, CO (2) NO, CO₂
(3) NH₃, PH₃ (4) NO, C₂H₆
- The rate of diffusion of methane at a given temperature is twice that of a gas X. The molecular weight of X is :
(1) 64 (2) 32 (3) 4.0 (4) 8.0
- The increasing order of effusion among the gases, H₂, O₂, NH₃ and CO₂ is –
(1) H₂, CO₂, NH₃, O₂ (2) H₂, NH₃, O₂, CO₂
(3) H₂, O₂, NH₃, CO₂ (4) CO₂, O₂, NH₃, H₂
- Gas A having molecular weight 4 diffuses thrice as fast as the gas B at a given T. The molecular weight of gas B is :
(1) 36 (2) 12 (3) 18 (4) 24
- Four rubber tubes are respectively filled with H₂, O₂, N₂ and CO₂. The tube which will be reinflated first is :
(1) H₂ filled tube (2) O₂ filled tube
(3) N₂ filled tube (4) CO₂ filled tube
- A balloon filled with methane CH₄ is pricked with a sharp point and quickly plunged into a tank of hydrogen at the same pressure. After sometime the balloon will have :
(1) Enlarged
(2) Collapsed
(3) Remained unchanged in size
(4) Ethylene (C₂H₄) inside it
- Rate of diffusion of hydrogen is :
(1) Half of He (2) 1.4 times of He
(3) Double than He (4) four times of He
- A football bladder contains equimolar proportions of H₂ and O₂. The composition by mass of the mixture effusing out of punctured football is in the ratio (H₂ : O₂)
(1) 1 : 4 (2) 2√2 : 1
(3) 1 : 2√2 (4) 4 : 1
- If the vapour densities of methane & oxygen are in the ratio 1 : 2, the ratio of rate of diffusion of O₂ & CH₄ is respectively
(1) 1 : 2 (2) 1 : 1.414
(3) 2 : 1 (4) 1.414 : 1
- A gas X diffuses three times faster than another gas Y the ratio of their densities i.e., D_x : D_y is
(1) 1/3 (2) 1/9
(3) 1/6 (4) 1/12
- The relative rate of diffusion of a gas (Mol wt. = 98) as compared to hydrogen will be :
(1) 1/7 (2) 1/5
(3) 1/4 (4) 1
- The relative rate of diffusion of a gas (molecular weight = 128) as compared to oxygen is
(1) 2 times (2) 1/4 times
(3) 1/8 times (4) 1/2 times
- Since the atomic weights of carbon, nitrogen and oxygen are 12, 14 and 16 respectively, among the following pairs of gases, the pair that will diffuse at the same rate is :
(1) Carbon dioxide and nitrous oxide
(2) Carbon dioxide and nitrogen peroxide
(3) Carbon dioxide and carbon monoxide
(4) Carbon dioxide and nitric oxide
- A bottle of dry ammonia and a bottle of dry hydrogen chloride connected through a long tube are opened simultaneously at both ends, the white ammonium chloride ring first formed will be :
(1) at the centre of the tube
(2) near the hydrogen chloride bottle
(3) near the ammonia bottle
(4) throughout the length of the tube
- 50 ml of a gas A diffuse through a membrane in the same time as for the diffusion of 40 ml of a gas B under identical pressure temperature conditions. If the Molecular weight of A = 64, that of B would be :
(1) 100 (2) 250
(3) 200 (4) 80
- If rate of diffusion of A is 5 times that of B, what will be the density ratio of A and B :
(1) 1/25 (2) 1/5
(3) 25 (4) 5
- 50 ml of hydrogen diffuses through a small hole from vessel in 20 minutes time. Time taken for 40 ml of oxygen to diffuse out under similar conditions will be :
(1) 12 min. (2) 64 min
(3) 8 min (4) 32 min
- The densities of two gases are in the ratio of 1 : 16. The ratio of their rates of diffusion is :
(1) 16 : 1 (2) 4 : 1
(3) 1 : 4 (4) 1 : 16
- The rate of diffusion of a gas having molecular weight just double of nitrogen gas is 56 ml per sec the rate of diffusion of nitrogen gas will be :
(1) 79.19 ml/sec. (2) 112 ml/sec
(3) 56 ml/sec (4) 90 ml/sec



20. If the four tubes of a car are filled to the same pressure with N_2 , O_2 , H_2 and CO_2 separately then which one will be filled first :

- (1) N_2 (2) O_2
(3) H_2 (4) CO_2

21. Under identical conditions of temperature and pressure the ratio of the rates of effusion of O_2 and CO_2 gases is given by :

- (1) $\frac{\text{rate of effusion of oxygen}}{\text{rate of effusion of } CO_2} = 0.87$
(2) $\frac{\text{rate of effusion of oxygen}}{\text{rate of effusion of } CO_2} = 1.17$
(3) $\frac{\text{rate of effusion of oxygen}}{\text{rate of effusion of } CO_2} = 8.7$
(4) $\frac{\text{rate of effusion of oxygen}}{\text{rate of effusion of } CO_2} = 0.117$

DEVIATION FROM IDEAL GAS BEHAVIOUR

22. When does a real gas show behaviour same as ideal gas:

- (1) At low temperature and low pressure
(2) At high temperature and high pressure
(3) At low temperature and high pressure
(4) At high temperature and low pressure

23. In van der Waal's equation of state of the gas law, the constant 'b' is a measure of :

- (1) intermolecular repulsions
(2) intermolecular attraction
(3) volume occupied by the molecules
(4) intermolecular collisions per unit volume

24. The term that accounts for intermolecular force in van der Waals' equation for non ideal gas is :

- (1) RT (2) $V - b$
(3) $\left(P + \frac{a}{V^2}\right)$ (4) $[RT]^{-1}$

25. Pressure of real gas is less than the pressure of ideal gas because :

- (1) No. of collisions increases
(2) Definite shape of molecule
(3) K.E. of molecule increases
(4) Inter molecular forces

26. Which gas can be easily liquefied ? given 'a' for $NH_3 = 4.17$, $CO_2 = 3.59$, $SO_2 = 6.71$, $Cl_2 = 6.49$

- (1) NH_3 (2) Cl_2
(3) SO_2 (4) CO_2

27. At relatively high pressure, van der waals' equation reduces to :

- (1) $PV = RT$ (2) $PV = RT + \frac{a}{V}$
(3) $PV = RT + Pb$ (4) $PV = RT - \frac{a}{V^2}$

28. A real gas most closely approaches the behaviour of an ideal gas at :

- (1) 15 atm and 200 K (2) 1 atm and 273 K
(3) 0.5 atm and 500 K (4) 15 atm and 500 K

29. The compressibility factor of an ideal gas is :

- (1) 0 (2) 1
(3) 2 (4) 4

30. The compressibility of a gas is less than unity at STP therefore :

- (1) $V_m > 22.4 \text{ L}$
(2) $V_m < 22.4 \text{ L}$
(3) $V_m = 22.4 \text{ L}$
(4) $V_m = 44.8 \text{ L}$

31. The values of van der Waal's constant 'a' for the gases O_2 , N_2 , NH_3 and CH_4 are 1.360, 1.390, 4.170 and 2.253 $L^2 \text{ atm mol}^{-2}$ respectively. The gas which can most easily be liquefied is :

- (1) O_2 (2) N_2
(3) NH_3 (4) CH_4

EXERCISE-I (Conceptual Questions)

ANSWER KEY

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Ans. | 4 | 1 | 4 | 1 | 1 | 1 | 2 | 1 | 2 | 2 | 1 | 4 | 1 | 2 | 1 |
| Que. | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| Ans. | 1 | 2 | 2 | 1 | 3 | 2 | 4 | 3 | 3 | 4 | 3 | 3 | 3 | 2 | 2 |
| Que. | 31 | | | | | | | | | | | | | | |
| Ans. | 3 | | | | | | | | | | | | | | |



Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
 (C) If Assertion is True but the Reason is False.
 (D) If both Assertion & Reason are false.

- Assertion :-** The pressure of real gas is less than the pressure of ideal gas.
Reason :- The intermolecular forces of attraction in real gases are greater than those of ideal gas.
 (1) A (2) B (3) C (4) D
- Assertion :-** CO₂ gas will have higher rate of liquification then H₂ gas.
Reason :- Because CO₂ will have higher value of Z so higher inter molecular force of attraction.
 (1) A (2) B (3) C (4) D
- Assertion :-** For Vanderwaal real gas, in low pressure region equation of compressibility factor is $Z = 1 - \frac{a}{VRT}$.
Reason :- In low pressure region 'b' is negligible.
 (1) A (2) B (3) C (4) D
- Assertion :-** Gases having higher critical temperature can be liquified easily.
Reason :- because attractive forces are higher for gases having higher critical temperature
 (1) A (2) B (3) C (4) D
- Assertion :-** At critical condition value of compressibility factor is 3/8.
Reason :- At critical condition attraction forces dominates.
 (1) A (2) B (3) C (4) D
- Assertion :-** Critical temperature of CO₂ is 304K. If it is compressed at 320 K. Then it will not liquify.
Reason :- Volume decreases on increasing pressure at a given temperature.
 (1) A (2) B (3) C (4) D
- Assertion :** Value of PV increases linearly for real gas on increasing pressure at constant temprature.
Reason : PV for real gas does not depend on pressure when temprature is constant.
 (1) A (2) B (3) C (4) D
- Assertion :** Pressure of real gas is less then ideal gas.
Reason : Because attractive forces in real gases are more than ideal gas.
 (1) A (2) B (3) C (4) D

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
|------|---|---|---|---|---|---|---|---|--|
| Ans. | 1 | 3 | 1 | 1 | 2 | 2 | 4 | 1 | |

